Chemistry of the Polynuclear Metal Halides. 13. Mixed-Metal $M_6X_{12}{}^{n+}$ Species Containing Both Tantalum and Molybdenum

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A new series of mixed-metal cluster compounds containing tantalum and molybdenum was prepared. The new compounds, which may be considered as metal-substituted derivatives of the $(Ta_6Cl_{12})^{n+}$ clusters, were $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$, $[(C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$, and $[(C_2H_5)_4N]_2[(Ta_4Mo_2Cl_{12})Cl_6]$. In all cases the mixed-metal basic cluster units $(Ta_5MoCl_{12})^{3+}$ and $(Ta_4Mo_2Cl_{12})^{4+}$ were obtained by reduction of $TaCl_5$–$MoCl_5$ mixtures with aluminum in fused $NaAlCl_4$–$AlCl_3$ at 325 °C. Subsequent ion-exchange and solvent extraction procedures for separation of the individual species from the salt mixture and related clusters of the same structure and net ionic charge were moderately successful. Spectroscopic and magnetic data for the compounds, taking into account possible impurities, indicate that $[(Ta_5MoCl_{12})Cl_6]^{3-}$ and $[(Ta_4Mo_2Cl_{12})Cl_6]^{2-}$ are analogues of $[(Ta_6Cl_{12})Cl_6]^{4-}$ having 16 metal–metal bonding electrons, and $[(Ta_5MoCl_{12})Cl_6]^{2-}$ is the analogue of $[(Ta_6Cl_{12})Cl_6]^{3-}$ with 15 bonding electrons.

Introduction

Structural studies of the hexanuclear metal halide cluster species of niobium, tantalum, molybdenum, and tungsten have shown the basic units[1-9] are $M_6X_{12}{}^{n+}$ (with M = Nb or Ta, X = F, Cl, Br, I) and usually $M_6X_8{}^{4+}$ (M = Mo or W and X = Cl, Br, I). In a few exceptional cases the above generalization for the basic units M_6X_{12} when M = Nb, Ta and M_6X_8 when M = Mo, W has been violated. For example, tungsten has been observed in the $M_6X_{12}{}^{6+}$ cluster,[10] and niobium has been observed in the $Nb_6I_8{}^{3+}$ cluster.[11-14] However, tantalum has never been observed in an M_6X_8 cluster unit, and molybdenum has only recently been found in the M_6X_{12} cluster unit.[15]

In view of the great stability of these metal halide cluster species, it seemed plausible that one metal atom could be substituted for another to create mixed-metal or "alloy" units without severely impairing the stability of the system. Such mixed-metal species were deemed highly desirable for certain purposes, viz., studies of electronic spectra and magnetic properties and the inferences that can be made about the metal–metal bonding in such highly electron-delocalized species. Niobium and tantalum previously have been reported to form mixed-metal cluster compounds of the type $Ta_{6-x}Nb_xBr_{14}$,[16] but here separation and study of discrete species were not achieved. In order to alter chemical properties more extensively, and hence provide easier separation of components of complex mixtures, the substituting metal atom should be chosen from a periodic group different from that of the metal of the unsubstituted cluster. This paper describes the preparation and characterization of the new compounds containing the mixed-metal moieties $Ta_{6-x}Mo_xCl_{12}$ where x = 1 or 2.

Experimental Section

Materials. Tantalum(V) chloride and molybdenum(V) chloride were prepared by combination of the elements in sealed evacuated tubes at 420 °C. High-purity aluminum(III) chloride was obtained by passing electronic grade (99.99% nominal purity) HCl over turnings of high-purity Al (99.99%) at 300 °C. All other reagents and solvents were of reagent grade and used without purification.

The 4Ta–2Mo(2–) Complex $[(C_2H_5)_4N]_2[(Ta_4Mo_2Cl_{12})Cl_6]$. Tantalum(V) chloride and molybdenum(V) chloride in equimol amounts were sealed in a Pyrex tube (10 cm length by 4 cm i.d.) along with enough aluminum to reduce the tantalum to Ta(2.33) and the molybdenum to Mo(2.0). Aluminum trichloride and sodium chloride in equimolar amounts were included to serve as a solvent for the reduction. In a typical reaction, 15 g of $TaCl_5$ (0.042 mol), 11.4 g of $MoCl_5$ (0.042 mol), 1.7 g of Al (0.063 g-atoms), 12.0 g of $AlCl_3$ (0.090 mol), and 6.1 g of NaCl (0.105 mol) were sealed in the tube. The sealed tube was wrapped in aluminum foil and then wrapped in a heating tape along with a chromel–alumel thermocouple. An outer wrapping of asbestos tape was applied, and the tube was shaken gently

for 3 days at 320 °C. The tube was then opened in air, and its contents were crushed with a mortar and pestle.

The crushed product was added bit by bit to 600–800 mL of water and stirred for 4 h in order to dissolve the $NaAlCl_4$, $AlCl_3$, and Ta_6Cl_{14}. The resulting mixture was centrifuged; the collected solids were extracted with water a second time for 2 h, and the solids were again centrifuged from the solution. An overnight extraction of the solids with 500 mL of absolute ethanol yielded a very dark, opaque solution which was centrifuged, filtered, and diluted with water to make the solvent about 25% water by volume. The ethanol–water solution was passed through a cation-exchange column (Dowex 50W-X8, 50–100 mesh, acid form) and transferred to a round-bottom flask. An ethanol solution of an excess of tetraethylammonium chloride was added; the solution was thoroughly flushed with argon, cooled in an ice bath, and saturated with anhydrous hydrogen chloride. About 6 h later 2.2 g of fine dark green crystals was collected on a glass frit, washed with absolute ethanol and ethyl ether, and air-dried. These crystals were soluble in acetonitrile and no changes were observed in the electronic spectrum of the solution when a portion of the solution was treated with either chlorine or zinc.

Anal. Calcd for $[(C_2H_5)_4N]_2[(Ta_4Mo_2Cl_{12})Cl_6$: Ta, 39.9; Mo, 10.6; C, 10.6; H, 2.22; Cl, 35.2. Found: Ta, 38.3; Mo, 10.5; C, 10.8; H, 2.25; Cl, 33.7.

The 5Ta–1Mo(2–) Complex $[(n\text{-}C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$. The general procedure for this compound was the same as for the preceding compound, but the proportion of the pentahalides in the starting mixture was altered to maximize the yield of 5–1 cluster over 4–2 cluster. In one specific reaction 25 g of tantalum(V) chloride (0.07 mol), 1.9 g of molybdenum(V) chloride (0.007 mol), 1.78 g of aluminum (0.066 g-atom), 14.4 g of aluminum trichloride (0.108 mol), and 4.3 g of sodium chloride (0.074 mol) were sealed into the reaction tube and shaken for 3.5 days at 320 °C. The product was extracted with 600 mL of water for 6 h, with 600 mL of water overnight, and then with 500 mL of absolute ethanol for 7 h. The solution was centrifuged, made 20% water by volume, and passed through Dowex 50W-X8 cation-exchange resin (50–100 mesh, acid form). Excess tetra-n-butylammonium chloride was added to the solution which was then cooled in an ice bath, flushed with argon, saturated with anhydrous hydrogen chloride, and allowed to stand overnight. A few crystals were filtered away from the mother solution. Then the solution was oxidized with chlorine and heated in air for 4 h. At that time 0.6 g of very dark fine crystals was collected on a glass frit and recrystallized from hydrogen chloride–saturated ethanol. The final yield was 0.5 g of dark red acicular crystals which seemed to be contaminated with about 10 mole % 4–2 cluster (from spectral data).

Anal. Calcd for $[(n\text{-}C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$: Ta, 42.2; Mo, 4.5; C, 18.0; H, 3.78. Found: Ta, 41.1; Mo, 5.0; C, 18.2; H, 3.56.

The 5Ta–1Mo(3–) Complex $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$. This compound can easily be obtained by reducing an acetonitrile solution of the 5–1(2–) compound with zinc. Conversely, the 5–1(3–) compound can be oxidized with chlorine in acetonitrile solution to obtain the 5–1(2–) compound. What follows is a description of a single experiment which afforded exceptionally pure 5–1 cluster, largely in the reduced form.

The products of three previous preparations which had yielded mixtures of about 70–80% 5–1 clusters and 20–30% 4–2 clusters were

combined in one acetonitrile solution. Metallic zinc was added, and the solution was allowed to stand for a week at room temperature. Some turbidity had appeared, but filtration restored the clarity of the solution. One gram of tetraethylammonium chloride in acetonitrile was added every few days until 10 g had been added. More turbidity appeared, and the solution was filtered through a glass frit under aspirator vacuum. This filtration step lowered the temperature of the effluent solution sufficiently to cause crystallization of spectrophotometrically pure $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$. A second crop of crystals was collected by evaporation of the mother solution under aspirator vacuum. An electronic spectrum showed this second crop of crystals to be contaminated with about 10% 4–2 cluster. The first crop of crystals was analyzed.

Anal. Calcd for $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$: Ta, 44.6; Mo, 4.73; Cl, 31.4; C, 14.2; H, 2.98. Found: Ta, 44.1; Mo, 4.77; Cl, 31.5; C, 13.7; H, 2.87.
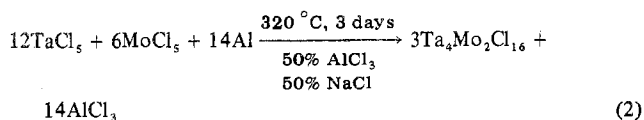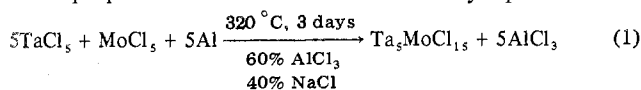
Analytical Procedures. Carbon, hydrogen, and molybdenum were determined by the Ames Laboratory Analytical Service Group, Iowa State University, Ames, Iowa. Total metal oxide was determined by reaction of the sample with nitric acid in the "H-tube" method.[17] Chlorine was determined by gravimetry as silver chloride or by potentiometric titration with standard silver nitrate after decomposition of the cluster compounds with hot aqueous potassium hydroxide.

Physical Measurements. Magnetic susceptibility measurements were made using the Faraday balance and the method described previously by Converse and McCarley.[18]

Far-infrared spectra on all samples were measured on Nujol mulls using polyethylene windows on a Beckman IR-11 spectrophotometer in the region 40–600 cm^{-1}. Electronic spectra were measured on acetonitrile solutions made up by dissolving weighed samples and diluting to volume in a volumetric flask. The solutions were contained in 1-cm fused quartz cells for measurement with a Cary Model 14 recording spectrophotometer using a solvent reference. A baseline was recorded for each spectrum so accurate absorbance values could be determined for any desired wavelength. The spectra obtained were resolved into Gaussian components using a computational method described previously by Fleming and McCarley.[19]

Results and Discussion

Synthesis and Separation of Mixed-Metal Species. This work represents the first preparation of mixed-metal M_6X_{12} or M_6X_8 clusters containing metals from different groups. The basic preparative reactions are described by eq 1 and 2.

$$5TaCl_5 + MoCl_5 + 5Al \xrightarrow[\substack{60\% \ AlCl_3 \\ 40\% \ NaCl}]{320\,^{\circ}C, \ 3 \ days} Ta_5MoCl_{15} + 5AlCl_3 \qquad (1)$$

$$12TaCl_5 + 6MoCl_5 + 14Al \xrightarrow[\substack{50\% \ AlCl_3 \\ 50\% \ NaCl}]{320\,^{\circ}C, \ 3 \ days} 3Ta_4Mo_2Cl_{16} + $$

$$14AlCl_3 \qquad (2)$$

When the reactions were performed without a solvent, no mixed-metal clusters were observed in the products. The solvent system NaCl–AlCl$_3$ was selected because of its wide liquid range, low vapor pressure, and variable acidity (as AlCl$_3$) over the temperature range desired. Although not substantiated by extensive data, an acidic solvent seemed to favor preparation of 5–1 clusters, while a neutral solvent favored preparation of the 4–2 cluster.

Preliminary reductions of the individual pentahalides by aluminum showed that the rate of reduction of each becomes appreciable at about 325 °C. A temperature of 310 °C was therefore selected for the first mixed-metal reductions in order to minimize the production of unmixed tantalum or molybdenum cluster species. This precaution was to no avail in preventing formation of tantalum cluster as $Ta_6Cl_{12}{}^{2+}$, but no molybdenum cluster was ever observed in the products except when molybdenum(V) chloride was originally present in large excess.

Additional reductions of the mixed pentahalides of tantalum and molybdenum showed that yields of all the clusters concerned dropped sharply if the reactions were carried out at temperatures of less than 300 °C or for times of less than 3

days. On the other hand, temperatures greater than about 320 °C and reaction times of longer than 3 days did little to improve the yields. The best yield of mixed-metal cluster ever obtained was 30% of the calculated amount; a more typical yield was ca. 15%.

Reaction time and temperature seemed to have little effect in determining which mixed-metal cluster was the major product. The most effective reaction variable in this regard was the Ta/Mo ratio in the starting mixture. Best results in preparing the 5–1 cluster were obtained with Ta/Mo = 8 to 10. Ratios greater than 10 resulted in small yields of mixed-metal clusters contaminated with large amounts of tantalum cluster. Ratios less than 8 resulted in greater contamination of the 5–1 cluster by the 4–2 cluster. When the 4–2 cluster was the desired product, a Ta/Mo ratio of 1 in the starting mixture gave the best results. Molybdenum cluster was observed as a product only when the Ta/Mo ratio in the starting mixture was lowered to 1/3, and even then some tantalum cluster was also prepared.

When the coreduction had been completed, most of the contaminating components could be leached out easily with water. The first of two water extractions of a finely crushed reduction mass removed most of the NaCl and AlCl$_3$ and hydrolyzed any higher tantalum or molybdenum halides present. This treatment also removed some of the tantalum cluster from the reaction product. The second water extraction completed the extraction of the water-soluble components of the mixture except for some of the tantalum cluster which was slow to dissolve. Total time for the two extractions was 6–10 h. Water extraction could be continued for several days to remove all the tantalum cluster present, but this treatment decreased the yield of mixed-metal clusters.

Extended water extraction could be avoided if an ion-exchange step was included to complete the removal of tantalum cluster. After the first two water extractions, the residue was extracted with absolute ethanol for 10–12 h to dissolve the mixed-metal compounds and any remaining tantalum cluster. The ethanol solution was made 20–25% water by volume and passed through Dowex 50W-X8 cation-exchange resin (acid form). Tantalum cluster (as either $Ta_6Cl_{12}{}^{2+}$ or $Ta_6Cl_{12}{}^{3+}$) was retained while the mixed-metal clusters passed through the column. Since in these solutions the mixed-metal clusters also passed through anion-exchange resins, it is assumed they are present as neutral species, e.g., $(Ta_5MoCl_{12})Cl_3$.

Since the detailed spectral data for compounds comparable to these mixed-metal clusters were largely on anionic cluster complexes, the mixed-metal clusters were isolated in anionic form. Isolation of the clusters as complex anions are provided for some fractionation of the mixture of mixed-metal clusters which was always obtained from the initial reaction. Anation of the mixture of mixed-metal clusters was carried out under nonoxidizing conditions so the subsequent fractionation would be of ions of different charge, viz., $[(Ta_4Mo_2Cl_{12})Cl_6]^{2-}$ and $[(Ta_5MoCl_{12})Cl_6]^{3-}$. Under these conditions the tetraalkylammonium salts of the 4–2 derivative were less soluble than those of the 5–1(3–) anion. Hence, the 4–2 derivative was concentrated in the first fraction of crystals. Normally, very little of the 5–1(3–) complex crystallized until the volume of the solution was reduced by about 30%. This treatment also caused further crystallization of the 4–2 derivative. Thus, the 4–2 derivative could usually be isolated in higher purity than the 5–1 derivatives.

The preparation of spectrophotometrically pure 5–1(3–) derivative as described in the Experimental Section leads to a potentially useful conclusion: in acetonitrile solution, the 5–1(3–) complex is apparently more stable toward solvolysis than is the 4–2 complex. Attempts to take advantage of this conclusion failed to uncover any set of conditions or time
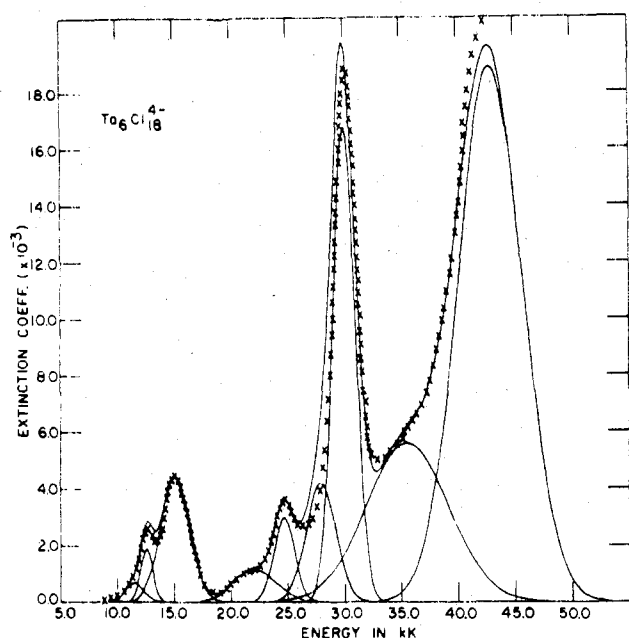
Figure 1. Spectrum of $[(Ta_6Cl_{12})Cl_6]^{4-}$ in acetonitrile showing observed (upper solid line), calculated (XXX), and Gaussian components (lower solid lines).

duration which would make the method useful as a routine purification procedure.

The complexes were usually isolated as tetraethylammonium salts. Several trial fractionations using other cations revealed no noticeable dependence of the success of the fractionation on the identity of the cation. The cesium salt $Cs_2[(Ta_5Mo-Cl_{12})Cl_6]$ was prepared by addition of CsCl to a solution of the 5–1(2–) complex in HCl-saturated ethanol and was obtained solely for the purpose of examining its far-infrared spectrum.

Electronic Spectra. From detailed studies of the electronic spectra of $Nb_6X_{12}^{n+}$ and $Ta_6X_{12}^{n+}$ derivatives[19] (X = Cl or Br, n = 2, 3, or 4) it has been concluded that all absorption bands in the region 5000 to ca. 30 000 cm^{-1} arise from transitions centered primarily on the cluster of six metal atoms. Attempts have been made to assign the bands in this region in terms of the transitions within the MO framework suggested by Cotton and Haas,[20] which classify the bonding MO's as A_{1g}, T_{1u}, T_{2g}, and A_{2u} and the antibonding MO's as T_{2g}, E_g, T_{2u}, T_{1g}, E_u, and T_{1u}. To say the least, these assignments are difficult to make because of the number of bands observed in the indicated region, the number of dipole-allowed transitions possible within the above MO framework, and uncertainties in the relative order of levels within both the bonding and antibonding sets.

Because many of the transitions observed in the above cases originate between doubly or triply degenerate states in O_h symmetry, it was thought that it might be helpful to break such degeneracies under lower symmetry and observe which bands in the spectra undergo splitting or major intensity changes. For transitions centered primarily on the metal atoms, introduction of a foreign metal atom should be most effective in lowering the symmetry. In the new species discussed here the $[(Ta_5MoCl_{12})Cl_6]^{n-}$ (n = 2 or 3) may be considered to have C_{4v} symmetry, and $[(Ta_4Mo_2Cl_{12})Cl_6]^{2+}$ may have either C_{2v} or D_{4h} symmetry depending on whether the Mo atoms have cis or trans configurations, respectively, in the octahedron.

The spectra of $[(Ta_5MoCl_{12})Cl_6]^{3-}$ and $[(Ta_4Mo_2Cl_{12})Cl_6]^{2-}$ should be compared with the spectrum of $[(Ta_6Cl_{12})Cl_6]^{4-}$ since these are formally isoelectronic species. The spectrum of $[(Ta_5MoCl_{12})Cl_6]^{2-}$ in the same way should be compared to that of $[(Ta_6Cl_{12})Cl_6]^{3-}$. Unfortunately, salts of $[(Ta_6Cl_{12})Cl_6]^{4-}$ are difficult to isolate because of their ease

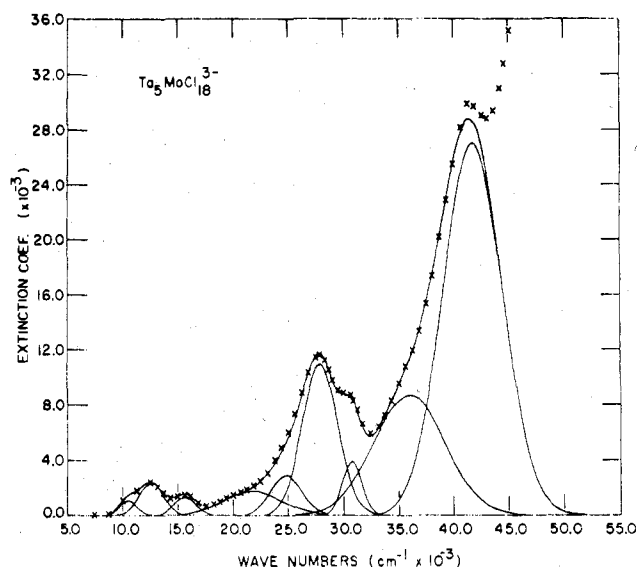**Figure 2.** Spectrum of $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$ in acetonitrile showing observed (upper solid line), calculated (XXX), and Gaussian components (lower solid lines).

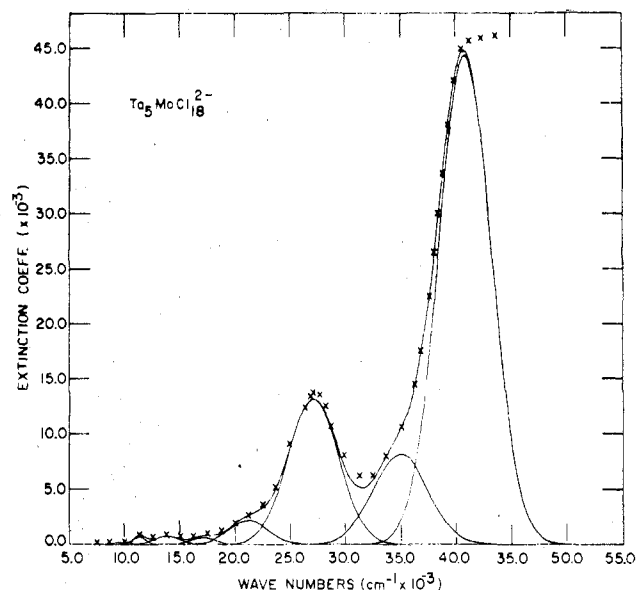**Figure 3.** Spectrum of $[(C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$ in acetonitrile showing observed (upper solid line), calculated (XXX), and Gaussian components (lower solid lines).

of oxidation to the 3– or 2– ions. Consequently, a solution containing the $[(Ta_6Cl_{12})Cl_6]^{4-}$ ion was obtained by sealing an acetonitrile solution of $[(C_2H_5)_4N]_2[(Ta_6Cl_{12})Cl_6]$ and a few granules of zinc in a spectrophotometer cell and heating the cell gently for about 2 h before measuring the spectrum. From the spectrum obtained it was concluded that reduction of the 2– ion to 4– was complete. Previous studies have established that in polar, aprotic solvents the chloro anions of these cluster species undergo little dissociation via substitution of solvent for chloride in the terminal coordination sites.[19,21]

The electronic spectra obtained here are shown in Figures 1–4. In each case the spectrum was analyzed by a fitting procedure described previously, and Gaussian component bands were obtained. A comparison of the component band energies for all of the related species is given in Figure 5. Parameters derived from the fitting procedure, including band maxima (ν), molar absorptivity (ϵ), and half-width at half-height (δ) are listed in Table I.

Two new features, previously unreported,[19] were discerned in the spectrum of $[(Ta_6Cl_{12})Cl_6]^{4-}$, viz., the band of low intensity at 1.149 μm^{-1} and the band of moderate intensity

Table I. Electronic Absorption Data[a]

[(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$			[(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{3-}$			[(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{2-}$			[(Ta$_4$Mo$_2$Cl$_{12}$)Cl$_6$]$^{2-}$		
ν^b	ϵ^c	δ^b	ν^b	ϵ^c	δ^b	ν^b	ϵ^c	δ^b	ν^b	ϵ^c	δ^b
11.49	0.67	0.94	10.40	1.10	0.93				8.84	0.15	0.79
12.56	1.91	0.62	12.54	2.58	1.28	9.67	0.22	0.72	10.30	1.29	0.52
15.06	4.46	1.51	15.55	1.36	1.11	13.69	0.76	1.30	11.24	0.59	0.45
						11.37	0.74	0.59	11.86	0.45	0.79
22.0	1.15	2.16	21.6	1.76	3.04	17.0	0.64	1.20	13.56	1.30	1.21
24.7	3.01	1.07	24.8	2.88	1.64	21.1	2.20	2.06	17.4	1.57	2.36
27.9	4.23	1.54	27.8	10.95	1.87				20.1	0.59	1.00
30.0	16.86	1.15	30.7	3.91	1.04	27.1	13.16	2.68	23.1	5.12	1.61
35.5	5.61	4.28	35.9	8.73	3.78	35.0	8.23	2.90	26.4	7.46	1.76
42.9	18.9	3.33	41.7	27.01	3.14	40.8	44.45	2.82	28.6	2.01	0.76
									29.9	4.50	2.91
									32.8	6.42	1.64
									39.2	17.61	4.48
									43.2	35.42	3.80
									46.9	30.61	1.88

[a] Absorptions are resolved Gaussian components. Spectra were obtained on acetonitrile solutions of tetraethylammonium salts. [b] In units of 10^3 cm^{-1}. [c] In units of L mol^{-1} cm^{-1} ($\times 10^{-3}$).
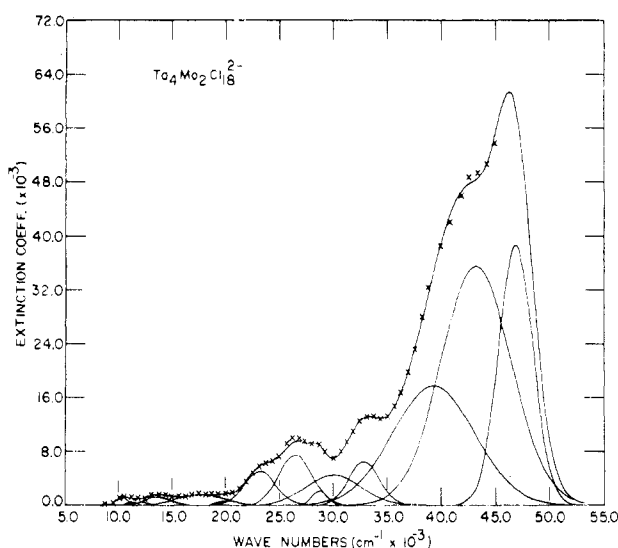

Figure 4. Spectrum of [(C$_2$H$_5$)$_4$N]$_2$[(Ta$_4$Mo$_2$Cl$_{12}$)Cl$_6$] in acetonitrile showing observed (upper solid line), calculated (×××), and Gaussian components (lower solid lines).

Figure 5. Comparison of component bands in spectra of the following: A, [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{3-}$ in acetonitrile;[18] B, (Ta$_6$Cl$_{12}$)$^{3+}$ in ethanol;[18] C, [(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{2-}$ in acetonitrile; D, [(Ta$_4$Mo$_2$Cl$_{12}$)Cl$_6$]$^{2-}$ in acetonitrile; E, [(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{3-}$ in acetonitrile; F, [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ in acetonitrile; G, [(Nb$_6$Cl$_{12}$)Cl$_6$]$^{4-}$ in acetonitrile.[18]

at 2.79 μm^{-1}. These bands were necessary to obtain good agreement between the observed and calculated spectrum; all attempts to fit the spectrum when these bands were deleted from the fitting procedure gave poor results. In the case of both bands it is not obvious from visual inspection of the spectrum that the component is present, and hence these components were easily overlooked in previous discussions for the Ta$_6$Cl$_{12}$$^{2+}$ spectrum. Without going into detail, we note that the presence of these bands indicates even greater discrepancies between the spectrum of Nb$_6$Cl$_{12}$$^{2+}$ and Ta$_6$Cl$_{12}$$^{2+}$ derivatives than previously deduced.[22]

However, with the inclusion of the two new bands for [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$, a remarkable one to one correspondence of component bands in the spectrum of this species with those in the spectrum of the isoelectronic [(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{3-}$ is observed as shown in Figure 5. Apparently substitution of one Mo for one Ta perturbs the spectrum insufficiently within the observed bandwidths for the band splitting under the lower symmetry to be discerned at ambient temperature. Although this is a disappointing result when viewed from a position of securing additional spectroscopic information, at the same time indication is given that the Mo atom enters into the delocalized bonding very effectively and virtually loses its identity as a discreet atom by doing so. The comparison of data given in Table I shows that the band positions generally are shifted by less than 0.1 μm^{-1} upon substitution of Mo into the cluster but that some major changes in relative intensities of the bands
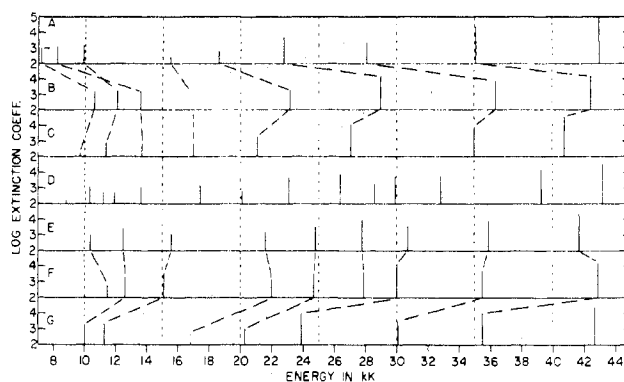
do occur.

Similarly the spectrum of [(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{2-}$ was found to bear a nearly identical relationship with the spectrum of (Ta$_6$Cl$_{12}$)$^{3+}$ derivatives, although the latter have not been subjected to a rigorous fitting procedure.[19] The sole discrepancy appears to be the band at 1.70 μm^{-1} in [(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{2-}$ which has no obvious analogue in the spectrum of (Ta$_6$Cl$_{12}$)$^{3+}$.

In view of the above observations the much greater complexity of the spectrum of [(Ta$_4$Mo$_2$Cl$_{12}$)Cl$_6$]$^{2-}$, which formally is isoelectronic with [(Ta$_6$Cl$_{12}$)Cl$_6$]$^{4-}$, is puzzling indeed. The interpretation of this spectrum is complicated by the possibility that the compound prepared consists of a mixture of cis and trans isomers. There is no reason to expect that the conditions used in the preparation (high temperature, fused salt) should lead to exclusive formation of one isomer or that the subsequent separation scheme should lead to any significant fractionation of isomers. Hence, it must be assumed that the spectrum does exhibit the bands of both isomers. However, it seems unreasonable that all of the "extra" bands found in this spectrum could arise solely from the mixture of isomers, per se. In view of the lack of resolved bands resulting from splitting of degenerate states under lower symmetry as noted for [(Ta$_5$MoCl$_{12}$)Cl$_6$]$^{3-}$, the resolution of so many bands resulting from differences in the symmetry of the cis and trans isomers of [(Ta$_4$Mo$_2$Cl$_{12}$)Cl$_6$]$^{2-}$ does not seem likely. Evidently substitution of two Mo atoms into the cluster causes a much stronger perturbation of the electronic structure than in the monosubstituted derivative, and band splitting resulting from the lower symmetry becomes observable. Before assignments of these bands are attempted, further studies of the spectra

Table II. Far-Infrared Spectra (cm⁻¹)ᵃ

Cs⁺ Ta₆- Cl₁₈²⁻ ᵇ	Cs⁺ Ta₅Mo- Cl₁₈²⁻	n-Bu₄N⁺ Ta₅Mo- Cl₁₈²⁻	Et₄N⁺ Ta₄Mo₂- Cl₁₈²⁻	Et₄N⁺ Ta₆- Cl₁₈³⁻ ᶜ	Et₄N⁺ Ta₅Mo- Cl₁₈³⁻
	348 sh	350 sh	348 vs, vb		352 sh
332 vs (F)	335 vs	336 vs		324 vs	326 vs
290 s (F)	296 m	300 s	303 s	283 vs	290 vs
	282 w	286 w			
253 vs (F)	254 vs	261 vs	260 vs	243 vs	245 vs
	200 w	202 m	202 s		197 m
	187 m	187 s	185 w		
165 m (F)		171 vw		171 w	
153 w	162 w	163 w		153 w	
141 s (F)	142 m	138 m	144 m	140 s	141 m
118 m (F)	122 m	122 w	124 m	118 m	123 m
53 m	55 m		70 m		

ᵃ Key: s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder. ᵇ (F) designates band as fundamental according to ref 23. ᶜ Data from ref 23.

at low temperature should be performed in order to gain resolution through reduction of bandwidths and to obtain a better estimate of the dipole strength of the transitions.

Magnetic Properties. Magnetic susceptibilities of the mixed-metal cluster compounds were measured over the range 77–298 K. Within experimental error all of the data conformed to Curie behavior. Although the magnetic susceptibility of the compounds $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$ and $[(C_2H_5)_4N]_2[(Ta_4Mo_2Cl_{12})Cl_6]$ were negative at room temperature (with $10^6\chi_M$ values of -301 and -331 emu/mol, respectively) both showed a temperature dependence from which magnetic moments of 0.76 and 0.42 μ_B, respectively, were calculated. Low magnetic moments such as these frequently are associated with paramagnetic impurities in diamagnetic compounds. Even though in the case of these two compounds good agreement was found between calculated and observed analytical data, the presence of small amounts of one paramagnetic cluster compound in the diamagnetic host would be difficult to detect from analytical data alone. Examples would be $[(Ta_5MoCl_{12})Cl_6]^{2-}$ as impurity in salts of $[(Ta_4Mo_2Cl_{12})Cl_6]^{2-}$, or $[(Ta_6Cl_{12})Cl_6]^{3-}$ as impurity in salts of $[(Ta_5MoCl_{12})Cl_6]^{3-}$. In the examples given, complete separation of impurities may be very difficult because of solid solution formation. Because the preparative procedures do lead to formation of mixtures of the cluster species and the subsequent separations are difficult at best, the low moments found in these two cases are reasonably attributed to such impurities. Thus we believe the two mixed-metal ions $[(Ta_5MoCl_{12})Cl_6]^{3-}$ and $[(Ta_4Mo_2Cl_{12})Cl_6]^{2-}$ are diamagnetic, and we assigned spin-singlet ground states like the isoelectronic $[(Ta_6Cl_{12})Cl_6]^{4-}$.[18]

The compound $[(C_4H_9)_4N]_2[(Ta_5MoCl_{12})Cl_6]$ is paramagnetic with $10^6\chi_M$ values (temperature, K) of 2900 (77), 979 (170), 966 (180), 749 (199), and 350 (296). From the slope of a Curie plot the magnetic moment of 1.47 μ_B is calculated. Also, from the EPR spectrum of the powder, the average g factor of 1.958 was obtained for this compound. With $\mu(\mu_B) = g[S(S + 1)]^{1/2}$, and assuming $S = 1/2$, the calculated magnetic moment is 1.69 μ_B. In this case diamagnetic impurities, such as $[(Ta_6Cl_{12})Cl_6]^{2-}$[18] or $[(Ta_4Mo_2Cl_{12})Cl_6]^{2-}$, apparently are present and cause the observed moment to be less than the value calculated from the measured g factor. However, it seems clear that the ion $[(Ta_5MoCl_{12})Cl_6]^{2-}$ contains one unpaired electron and thus may be considered as isoelectronic with $[(Ta_6Cl_{12})Cl_6]^{3-}$ or $[(Nb_6Cl_{12})Cl_6]^{3-}$.

Infrared Spectra. In the region 30–400 cm⁻¹ the infrared spectra arise from the vibrational modes of the cluster species. As in the case of the electronic spectra it is apparent that substitution of Mo atoms into the Ta_6Cl_{12} cluster unit causes little perturbation of the infrared-active vibrational modes. The

data presented in Table II illustrate this point quite well. In O_h symmetry, as with $[(Ta_6Cl_{12})Cl_6]^{n-}$,[23] only six infrared-active T_{1u} modes (fundamentals) are permitted. These six fundamental bands (F) are identified in Table II for the compound $Cs_2[(Ta_6Cl_{12})Cl_6]$. By comparison the ions $[(Ta_5MoCl_{12})Cl_6]^{n-}$ in C_{4v} symmetry should exhibit 30 infrared-active fundamentals; the ion $[(Ta_4Mo_2Cl_{12})Cl_6]$ in D_{4h} symmetry should exhibit 16 IR modes, and in C_{2v} symmetry, 54 IR modes. However, in the spectra of the mixed-metal species only a few of the expected bands are observed, and the most intense of these correspond to the fundamentals identified for the unmixed species of O_h symmetry.

As found in the case of the $[(Ta_6Cl_{12})Cl_6]^{n-}$ species,[23] increasing oxidation (decreasing net charge) of the mixed-metal anions causes significant shift of the bands above 200 cm⁻¹ to higher wavenumber, while the bands below this energy undergo little change. The striking similarity of the spectra between the mixed- and unmixed-metal species again leaves little doubt that all have the same basic structure.

Conclusions

The results reported here show that metal atoms from a different periodic group may be substituted into the Ta_6Cl_{12} cluster unit. In the cases considered it was found that the cluster unit undergoes a formal charge adjustment in order to attain the status of a full complement of 16 electrons in the metal–metal bonding levels and an empty set of antibonding orbitals. Since each Mo atom carries one more electron than Ta, as Mo atoms replace Ta the formal charge of the cluster increases. Thus the pseudo-isoelectronic series was established as $(Ta_6Cl_{12})^{2+}$, $(Ta_5MoCl_{12})^{3+}$, and $(Ta_4Mo_2Cl_{12})^{4+}$. Also it was found that the $(Ta_5MoCl_{12})^{3+}$ ion could be oxidized to $(Ta_5MoCl_{12})^{4+}$, which is analogous to $(Ta_6Cl_{12})^{3+}$ with 15 electrons in metal–metal orbitals. However, under the conditions investigated here no evidence was found for further oxidation to $(Ta_5MoCl_{12})^{5+}$, which would be the 14-electron analogue of $(Ta_6Cl_{12})^{4+}$. Likewise, no evidence was found for oxidation of $(Ta_4Mo_2Cl_{12})^{4+}$. Thus, it appears that for these $M_6X_{12}^{n+}$ cluster species the maximum formal charge is 4+.

An interesting question arises regarding the extension of the $(Ta_{6-x}Mo_xCl_{12})^{n+}$ series to values of $x > 2$. With $x = 3$ one might expect $(Ta_3Mo_3Cl_{12})^{5+}$, but an alternate possibility would be for conversion to the more stable $M_6X_8^{n+}$ cluster arrangement, as typified by derivatives of $(Mo_6Cl_8)^{4+}$, with 24 electrons in metal–metal bonding orbitals. Hence, for $x > 2$, completion of the series might result in the species $(Mo_3Ta_3Cl_8)^{+}$, $(Mo_4Ta_2Cl_8)^{2+}$, and $(Mo_5TaCl_8)^{3+}$. In the present study no evidence was found for any mixed-metal species with $x > 2$, even though reaction mixtures with Mo/Ta = 1 were investigated. This result may not be surprising in view of the apparent hindered formation of the $M_6X_8^{4+}$ clusters (M = Mo or W; X = Cl or Br) in the same fused salt melts at temperatures below 400 °C, as established in this laboratory.[24] Further work to extend the Ta–Mo mixed-metal clusters to species with $x > 2$ and to prepare clusters with other combinations of metal atoms presently is in progress.

References and Notes

(1) H. Schafer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).
(2) J. Lewis, *J. Pure Appl. Chem.*, **10**, 11 (1965).
(3) F. A. Cotton, *Q. Rev., Chem. Soc.*, **20**, 389 (1966).
(4) R. V. Parrish, *Adv. Inorg. Chem. Radiochem.*, **9**, 315 (1966).
(5) D. L. Kepert and K. Vrieze in "Halogen Chemistry", Vol. 3, V. Gutmann, Ed., Academic Press, New York, N.Y., 1967, p 10; F. Fairbrother, *ibid.*, p 123; J. E. Fergusson, *ibid.*, p 227.
(6) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).
(7) B. J. Bulkin and C. A. Rundell, *Coord. Chem. Rev.*, **2**, 37 (1967).

(8) B. R. Penfold, *Perspect. Struct. Chem.*, **2**, 71 (1968).
(9) F. A. Cotton, *Acc. Chem. Res.*, **2**, 240 (1969).
(10) R. Siepman, H. G. Schnering, and H. Schafer, *Angew Chem., Int. Ed. Engl.*, **6**, 637 (1967).
(11) D. Bauer, H. G. Schnering, and H. Schafer, *J. Less-Common Met.*, **8**, 388 (1965).
(12) A. Simon, H. G. Schnering, H. G. Wohrle, and H. Schafer, *Z. Anorg. Allg. Chem.*, **339**, 155 (1965); A. Simon, H. G. Schnering, and H. Schafer, *ibid.*, **355**, 295 (1967).
(13) L. R. Bateman, J. F. Blount, and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1082 (1966).
(14) M. A. Kust, J. D. Corbett, and R. M. Friedman, *Inorg. Chem.*, **7**, 2081 (1968).

(15) D. L. Kepert, R. E. Marshall, and D. Taylor, *J. Chem. Soc., Dalton Trans.*, 506 (1974).
(16) H. Schafer and B. Spreckelmeyer, *J. Less-Common Met.*, **11**, 73 (1966).
(17) H. Schafer and K. Dohman, *Z. Anorg. Allg. Chem.*, **300**, 1 (1959).
(18) J. G. Converse and R. E. McCarley, *Inorg. Chem.*, **9**, 1361 (1970).
(19) P. B. Fleming and R. E. McCarley, *Inorg. Chem.*, **9**, 1347 (1970).
(20) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).
(21) R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, **6**, 549 (1967).
(22) D. J. Robbins and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 2350 (1972).
(23) P. B. Fleming, J. L. Meyer, W. K. Grindstaff, and R. E. McCarley, *Inorg. Chem.*, **9**, 1769 (1970).
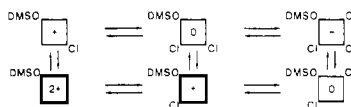(24) W. C. Dorman and R. E. McCarley, *Inorg. Chem.*, **13**, 491 (1974).

Kinetics and Mechanism for Ligand Substitution Reactions of Square-Planar (Dimethyl sulfoxide)platinum(II) Complexes. Stability and Reactivity Correlations

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The 14 rate constants in the system (aqua ligands excluded)

have been determined at 25.0 °C and in 1.00 M perchloric acid medium using both stopped-flow and conventional spectrophotometry. The equilibrium constants have been obtained from the rate constants, and three of them, also from independent spectrophotometric equilibrium measurements. The overall stability constants for the complexes Pt-$(DMSO)Cl_j(H_2O)_{3-j}^{2-j}$, $j = 1, 2, 3$, are $\beta_1 = (1.20 \pm 0.12) \times 10^6$ M^{-1}, $\beta_2 = (3.2 \pm 1.1) \times 10^{10}$ M^{-2}, and $\beta_3 = (5.8 \pm 2.9) \times 10^{12}$ M^{-3}. Comparisons of thermodynamic and kinetic parameters for the reactions in this system with corresponding reactions of similar complexes have been used to distinguish between the cis and trans influence and the cis and trans effect for DMSO compared to other ligands. The cis and trans influences, obtained from comparisons of equilibrium constants, are related to energy differences between complexes in their ground states, while the cis and trans effects, obtained from comparisons of rate constants, are related to energy differences between transition states and ground states. A quantitative evaluation of these contributions to the reactivity gave the trans influence order $H_2O \approx Cl^- \approx Br^- < C_2H_4 \approx DMSO < NH_3$ (1:1:1:3:4:10) and the cis influence order $DMSO \approx C_2H_4 < Br^- \approx Cl^- \approx H_2O < NH_3$ (0.1:~0.3:1:1:1:1–2). Thus, DMSO destabilizes trans chlorides by a factor of about 4 and stabilizes cis chlorides by a factor of about 10 compared to water. These thermodynamic influences are small compared to the (kinetic) trans effects, which are in the order $H_2O < NH_3 < Cl^- < Br^- < DMSO < C_2H_4$ (1:200:330:3000:2 × 10^6:~10^{11}). The (kinetic) cis effects are generally much smaller than the trans effects and are approximately $C_2H_4 < Br^- \approx Cl^- < NH_3 \approx H_2O < DMSO$ (0.05:0.3:0.4:1:1:5). Thus, DMSO has an intermediate trans effect and a relatively large cis effect compared to other ligands. Activation parameters for some reactions have been determined. The variation of activation entropies indicates that the ionic charge of the substrate complex is also an important factor for the rates of halide anation reactions. It appears that both the stability and reactivity of simple square-planar complexes can be described by empirical relationships with a small number of parameters. The stability constant for $Pt(DMSO)(H_2O)_3^{2+}$ is at least 10^7 M^{-1}.

Introduction

In aqueous solution, dimethyl sulfoxide (DMSO) reacts with tetrachloroplatinate(II) forming a strong, sulfur-bonded 1:1 complex which can be prepared in the solid state as the potassium salt $KPt(DMSO)Cl_3$.[1] Isotopic exchange studies have indicated that the exchange of the trans chloride in Pt-$(DMSO)Cl_3^-$ is "instantaneous" whereas the cis chlorides are exchanged slowly.[2] Hydrolysis products of the aqua complexes $Pt(DMSO)(H_2O)Cl_2$, *cis*-$Pt(DMSO)(H_2O)_2Cl^+$, and Pt-$(DMSO)(H_2O)_3^{2+}$ have been prepared by equilibration of aqueous solutions of $Pt(DMSO)Cl_3^-$ in the presence of excess silver(I) ion.[3-5] Kukushkin[6] has reviewed these investigations.

We here report a complete kinetic and equilibrium study of the platinum(II)–DMSO–chloro–aqua system. Comparisons of thermodynamic and kinetic parameters for the reactions in this system with corresponding reactions in the platinum(II)–chloro–aqua system studied previously[7] and with reactions of other similar complexes, such as $Pt(C_2H_4)Cl_3^-$, can be used to distinguish between the trans and cis influence and the trans and cis effect for DMSO compared to other

ligands. It also enables a quantitative evaluation of these contributions to the reactivity of the complexes.

Reaction Model and Rate Expressions

The kinetic scheme in Figure 1 (eq 1–7) is applicable. Rate constants for chloride anations are denoted k_n and for acid
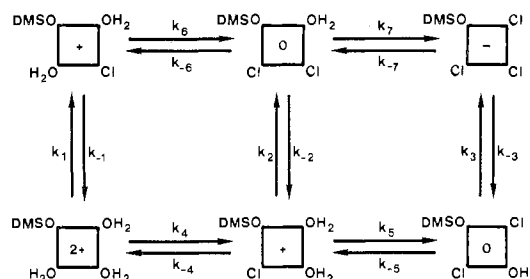

Figure 1. Reaction model. Rate constants for chloride anations are denoted k_n and for acid hydrolyses k_{-n}, $n = 1, 2, ..., 7$. Vertical arrows denote very fast substitutions of ligands trans to DMSO and horizontal arrows comparatively slow reactions.